# Characterization of the dissociation of acetonitrile on gold from a non-aqueous solution using surface-enhanced Raman spectroscopy

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The discovery of the giant surface-enhanced Raman scattering (SERS) from pyridine adsorbed at silver electrode in the mid. of 1970s has presented the electrochemists with a potentially powerful technique for probing the electrode-electrolyte interface in-situ. Most of the SERS studies were carried out in aqueous systems. Relatively smaller attention has been received in the study of non-aqueous systems not only because of the interference of the organic solvent but of the low detection sensitivity of the Ramanor. The advent of confocal microprobe Ramanor these years, however, has made it possible to probe the electrochemical/chemical process occurring at the metal/non-aqueous solution interface.

Acetonitrile is probably one of the widely used organic solvents. The electrochemical redox characteristic and adsorption behavior of acetonitrile in aqueous solution at noble metals such as Ag, Au, Pt etc. have been widely investigated using spectroelectrochemical techniques. No consensus, however, has been received for the different environments and conditions used by the researchers. In this contribution, we reported the adsorption and dissociation of acetonitrile on Au electrode as a solvent from the nonaqueous solution.

A set of potential-dependent surface Raman spectra on the gold electrode in acetonitrile solution with 0.1 M $LiClO_4$ was given in Fig 1. All potentials quoted refer to the Ag / $Ag^+$ reference electrode (0.268 V vs. SCE). No signal was observed at the initial potential of -0.2 V. On scanning potential negatively to -0.3 V, a new band centered at ca. 2137$cm^{-1}$ appeared. Its frequency downshifted sequentially and band intensity got its maximum value at about -1.5 V. This band did not disappear until about -2.1 V. The spectral behavior with electrode potential is quite similar to that observed from cyanide ions adsorbed at Au electrode in the aqueous solution [1], which indicates the formation of $CN^-$ in the present study. A dissociation reaction of acetonitrile at roughened gold surface was thus reasoned. This phenomenon has also been observed on silver[2] and Pt electrode[3] in non-aqueous solution and copper[4] in aqueous one. Therefore, one can assume that the acetonitrile may dissociate to cyanide firstly and the formation of $CN^-$-Au complex would occur leading to the changes of the Raman spectra with potential. Many factors found in our experiments, including laser illumination, solution pH, and trace water in the system may influence this process. A systematic investigation is still on in our laboratory.

References:

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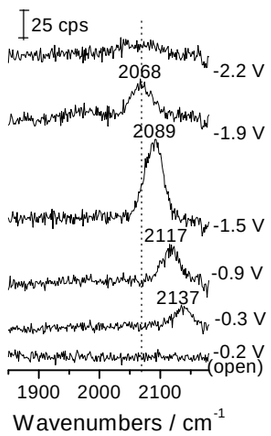


Fig.1 Potential-dependent SER spectra from the gold electrode in 0.1 M $LiClO_4$ / $CH_3CN$. Acquisition time:10s, laser wavelength: 632.8 nm.

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